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Vibrational and electronic absorption spectra of 2,3- and 2,4-difluorobenzaldehydes

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Abstract : Raman, infrared and electronic absorption spectra have been observed for 2,3- and 2,4- difluorobenzaldehydes and vibrational analysis has been made.

Keywords : Raman and infrared spectra, electronic absorption, vibrational analysis.

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Many investigators have studied the ultraviolet, infrared and Raman spectra of benzaldehyde and their derivatives (Buraway and Chamberlain 1952, Chandra and Sharma 1963, Garg, 1953-54, Imanishi *et al* 1952, Jaiswal 1969, Jaiswal and Sharma 1969, Morton and Stubs 1941, Padhye *et al* 1961, Patel 1959, Rao and Rao 1960, Robinson 1954, Singh and Juyal 1965). In benzene and substituted benzenes, the electronic system $^1B_{2u} \leftarrow {}^1A_{1g}$ (2600 Å) has been studied in great detail. In substituted benzenes $^1B_{1u} \leftarrow {}^1A_{1g}$ (2100 Å) transition has not been studied much in vapour phase. Because of the few studies on the second system, it was felt that a continuation of the studies of electronic, infrared and Raman spectra of some more trisubstituted benzenes would be worthwhile, as this would give some insight into the structure of the molecules in their ground and excited states. As a part of our research programme, the present note reports the vibrational analysis of the Raman spectra, infrared and electronic absorption spectra of 2,3- and 2,4- difluorobenzaldehydes.

The experimental techniques used to record the vapour absorption electronic spectra and infrared and Raman spectra in the pure liquid phase and accuracy in the positions of the bands reported are the same as given in our earlier work (Shashidhar 1971).

2,3- and 2,4-difluorobenzaldehydes may be considered as belonging to the point C_s, if we consider -CHO group to behave as a single mass point and coplanar with the benzene ring. The total number of 36 normal modes of vibration will have the distribution 25a' + 11a". The Raman and infrared absorption spectra have been analysed keeping in view of the symmetry of the molecules, the analysed infrared and Raman data of benzaldehyde and substituted benzaldehydes. It must however be emphasized that many modes are considerably mixed precluding in fact, the use of terms such as stretching or deformation. It

Table 1. Fundamental vibrational frequencies cm^{-1} of 2,3- and 2,4-difluorobenzaldehyde.

Wave number (cm^{-1}) and intensity**								C_s symmetry species	Description of mode*
2,3-difluorobenzaldehyde				2,4-difluorobenzaldehyde					
IR	Raman	Electronic		IR	Raman	Electronic			
		ground state	excited state			ground state	excited state		
—	—			—	123ms			a"	o.p CHO torsion
240m	235mw	—	183ms (175ms)	—	223m	—	186ms	a"	X-sensitive
255mw	252w			255m	260mw			a"	X-sensitive
290mw	294w			295mw	290mw			a"	X-sensitive
315mw	319m	315mw	254mw	310ms	310s	318m	291s	a'	X-sensitive
375w	375sh	370mw	284s	375s	375m	379mw	328s (342s)	a'	X-sensitive
440w	432w			455s	460m			a"	X-sensitive
470mw	470m	—	375s (351s)	490s	485ms	—	381ms	a'	X-sensitive
530m	535mw	—	493s	525s	520s	—	450ms	a'	X-sensitive
545w	540w			545sh	—			a"	C-C o.p.b.
605m	605mw	—	530m (511ms)	615s	615s	—	556m	a'	C-C i.p.b.
630m	630m			630vs	625s			a"	C=O o.p.b. in CHO group
700s	700m	—	640ms	720s	715s	—	630ms	a'	X-sensitive
715s	—			690ms	690m			a"	C-C o.p.b.
765ms	772s	—	750ms (726ms)	800vs	800s	—	698s (682s)	a'	X-sensitive
790s	798s			815sh	812m			a"	C-H o.p.b.
860m	865mw			845s	—			a"	C-H o.p.b.
900ms	910w			965vs	958s			a"	C-H o.p.b.
1012s	—			1005ms	—			a"	C-H o.p.b. wagging in CHO group

Table 1. *(Contd.)*

Wave number (cm^{-1}) and intensity[++]									
2,3-difluorobenzaldehyde				2,4-difluorobenzaldehyde				C_s symmetry species	Description of mode[+]
IR	Raman	Electronic		IR	Raman	Electronic			
		ground state	excited state			ground state	excited state		
1065s	1060m	—	994m	1080s	1085ms	—	991ms	a'	C-H i.p.b.
1165s	—	—	1095ms	1125s	1130ms	—	1032ms	a'	C-H i.p.b.
1180sh	—	—	1141ms (1137ms)	1170s	1175ms	—	1084s (1068s)	a'	X–sensitive
1220s	—	—	1177ms	1240s	1235vs	—	1135s	a'	X–sensitive
1245s	—	—	1226s (1231ms)	1260s	1260s	—	1234s (1214s)	a'	X–sensitive
1270s	1265ms			1300ms	1305ms			a'	C-H i.p.b.
1335ms	—	—	1297ms	1310ms	1315m	—	1270s	a'	C-C stretch
1400s				1400s	1400m			a'	C-H i.p.b. in CHO group
1480s	1480m			1425s	1425mw			a'	C-C stretch
1510mw				1480s	1485ms			a'	C-C stretch
1595s				1590s	1595vs			a'	C-C stretch
1620s	1615s		(1421s)	1620sh	1625mw		(1386s)	a'	C-C stretch
1705s	1710s			1750s	1712vs			a'	C-O stretch in CHO group
2770s	2775ms			2750s	—			a'	C=O stretch in CHO group
3030m	3040m			3090m	—			a'	C-H stretch
3060ms	3065m			3070sh	—			a'	C-H stretch
3090s	3085m			3120s	—			a'	C-H stretch

[++] Letters infront wave numbers represent the visual intensities of the bands observed.

mw = medium weak; ms = medium strong; s = strong; vs = very strong; m = medium; w = weak; sh = shoulder; x = substituent; ( ) = values from $^1B_{1u} \leftarrow {}^1A_{1g}$ system, + o.p. = out-of-plane; o.p.b. = out-of-plane bend; i.p.b. = in-plane bend.

might be noted that a ring stretch also implies a certain amount of C-H deformation and vice versa. Thus with some assignments, a certain vibration turns out to be predominently a stretch or a deformation whereas in others this might not be the case. The fundamental vibrational frequencies so chosen are listed in Table 1, along with their assignments.

The electronic absorption spectra of 2,3- and 2,4- difluorobenzaldehydes show two π^* $\leftarrow \pi$ systems, one consisting of rather well defined bands around 2900 Å (System I) and the other having some weak bands around 2300 Å (System II). Even under the widely varied experimental conditions with the spectrographs used, it was not possible to improve the System II. So this system was also recorded on a Hitachi U-3200 UV/VIS spectrophotometer in vapour phase and in this record, some bands were observed in the region 2300 to 2100 Å. The System I has been identified as corresponding to the forbidden electronic transition $^1B_{2u} \leftarrow {}^1A_{1g}$ and the System II to the transition $^1B_{1u} \leftarrow {}^1A_{1g}$ of benzene.

Ultraviolet spectra of System I of the molecules lie approximately in the region 2900 Å. The effect of temperature on the band system has facilitated the choice of the bands at 33750 cm^{-1} and 35445 cm^{-1} as the 0, 0 band in 2,3- and 2,4-difluorobenzaldehyde respectively. The identification of the fundamentals chosen in compounds has been done mainly on the basis of intensities of the bands and the available literature on the analyses of other trisubstituted benzenes. The strong bands on the longer wavelength side with spacing 68 cm^{-1} and 66 cm^{-1} in 2,3- and 2,4-difluorobenzaldehydes have been identified as sequence intervals. The band data are with the authors. The analysis of the electronic spectra of the molecules shows a red shift in the order of 2,3- > 2,4-difluorobenzaldehyde with respect to benzene. Such a trend has also been reported in literature (Padhye and Varadarajan 1963).

In System II, bands observed towards the longer wavelength side at 41706 cm^{-1} and 41654 cm^{-1} in 2,3- and 2,4-difluorobenzaldehydes have been identified as 0, 0 bands. The identified excited state fundamentals are also listed in Table 1 and they are correlated to the fundamentals of System I. The existence of such a System II has been reported in the literature (Amma *et al* 1969, Goel and Agarwal 1982).

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